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Sir:

Transmitted herewith for filing is the Patent Application (37 CFR 1.53(b)) in the name(s) of:  
**Toshikazu HAMAMOTO, Akira UEKI, Koji ABE and Yasuo MATSUMORI**

**FOR: NON-AQUEOUS ELECTROLYTIC SOLUTION AND LITHIUM SECONDARY BATTERY**

**ENCLOSED ARE:**

- (X) 19 pages of Specification, 5 pages of Claims (# of claims 29) & Abstract;
- ( ) Figs. / ( ) sheet(s) of Drawings;
- (X) Declaration and Power of Attorney;
- (X) Assignment to: *Ube Industries, Ltd. with PTO-1619A*;
- ( ) Foreign priority(ies) of *Japanese Pat.Appln Nos. 11-143222 filed May 24, 1999 and 2000-116327 filed April 18, 2000*; the priority(ies) of which is(are) claimed under 35 USC 119; **TO FOLLOW**
- ( ) Verified Statement to establish Small Entity Status (37 CFR 1.9 & 1.27);
- ( ) Information Disclosure Statement, PTO-1449 and \_\_\_ reference(s);

**THE FILING FEE HAS BEEN CALCULATED AS SHOWN BELOW:**

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Respectfully submitted

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NON-AQUEOUS ELECTROLYTIC SOLUTION  
AND LITHIUM SECONDARY BATTERY

FIELD OF THE INVENTION

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The present invention relates to a non-aqueous electrolytic solution favorably employable for a non-aqueous lithium secondary battery.

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BACKGROUND OF THE INVENTION

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At present, a non-aqueous secondary battery such as a lithium secondary battery (particularly, lithium ion secondary battery) is generally employed as an electric source for driving a small electronic device. The non-aqueous secondary battery comprises a positive electrode, a non-aqueous electrolytic solution, and a negative electrode. The non-aqueous lithium ion secondary battery preferably comprises a positive electrode of lithium complex oxide such as  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , or  $\text{LiNiO}_2$ , a non-aqueous electrolytic solution such as a solution of electrolyte in a carbonate solvent such as ethylene carbonate (EC) or propylene carbonate (PC), and a negative electrode of carbonaceous material or lithium metal. Recently, the carbonaceous material such as coke or graphite has been paid much attention, because a negative electrode of carbonaceous material hardly forms thereon deposition of lithium metal in the form of dendrite and therefore hardly produces an electric short circuit with a positive electrode. Further, no liberation of lithium metal from the negative electrode occurs.

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The non-aqueous secondary battery preferably has good battery characteristics such as large electric discharge capacity and high electric discharge retention. For instance, in a non-aqueous lithium ion secondary battery using a positive electrode of  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , or

LiNiO<sub>2</sub>, oxidative decomposition of a portion of the non-aqueous electrolytic solution undergoes in the electric charging stage. The decomposition product disturbs electrochemical reaction so that the electric discharge capacity decreases. It is considered that the oxidative decomposition takes place in the non-aqueous solvent of the non-aqueous electrolytic solution on the interface between the positive electrode and the electrolytic solution.

Moreover, in a non-aqueous lithium ion secondary battery using negative electrode of carbonaceous material of high crystallinity such as natural graphite or artificial (or synthetic) graphite, reductive decomposition of the solvent of the non-aqueous electrolytic solution undergoes on the surface of the negative electrode in the charging stage. The reductive decomposition on the negative electrode undergoes after repeated charging-discharging procedures even in the case of using a cyclic carbonate such as ethylene carbonate (EC) and propylene carbonate (PC) which is a preferably employed solvent of the electrolytic solution.

#### SUMMARY OF THE INVENTION

It is an object of the present invention to provide a non-aqueous electrolytic solution which is favorably employable for the preparation of a non-aqueous lithium secondary battery, particularly a non-aqueous lithium ion secondary battery.

It is another object of the invention to provide a non-aqueous secondary battery such as a lithium ion secondary battery which has improved discharge capacity retention.

The present invention resides in a non-aqueous electrolytic solution comprising at least two organic compounds dissolved in a solvent comprising a cyclic carbon-

ate and a chain carbonate, in an amount of 0.01 to 8 weight % (preferably, 0.1 to 4 weight %) for each organic compound,

5 in which both of said two organic compounds have a reduction potential higher those of the cyclic and chain carbonates, and

10 in which said one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.4 V (preferably less than 0.2 V).

15 In the non-aqueous electrolytic solution of the invention, the one organic compound preferably has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.05 V.

20 The invention further resides in a non-aqueous secondary battery which comprises a positive electrode comprising lithium complex oxide, a negative electrode comprising graphite, a non-aqueous electrolytic solution containing an electrolyte salt in a non-aqueous solvent, and a separator, in which the non-aqueous electrolytic solution comprises at least two organic compounds dissolved in a solvent comprising a cyclic carbonate and a chain carbonate, in an amount of 0.01 to 8 weight % (preferably, 0.1 to 4 weight %) for each compound, in which both of said two organic compounds have a reduction potential higher than those of the cyclic and chain carbonates, and in which said one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.4 V (preferably less than 0.2 V).

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#### DETAILED DESCRIPTION OF THE INVENTION

The present invention is described below in more detail.

5 The present invention is characterized by incorporation of at least two organic compounds into a solvent comprising a cyclic carbonate and a chain carbonate, in an amount of 0.01 to 8 weight % (preferably, 0.1 to 4 weight %) for each compound. Both of the two organic compounds have a reduction potential higher than those of  
10 the cyclic and chain carbonates, and one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.4 V (preferably less than 0.2 V, more preferably  
15 less than 0.05 V).

The above-mentioned two or more organic compounds are preferably selected from the group consisting of a carbonate compound, a sultone compound, a sulfonate compound, a sulfone compound, and phenyl acetylene.

20 Examples of the carbonate compounds include vinylene carbonate, methyl propargyl carbonate, and benzaldoxime carbonate.

Examples of the sultone compounds include 1,3-propanesultone and 1,4-butanedisultone.

25 Examples of the sulfonate compounds include 1,4-butanediol dimethane sulfonate and ethylene glycol dimethane sulfonate.

Examples of the sulfone compounds include divinyl sulfone.

30 The two or more organic compounds are preferably employed in such manner that one organic compound is a carbonate compound, and another organic compound is a sultone compound, a sulfonate compound, or a sulfone compound. Particularly, it is preferred that one organic  
35 compound is vinylene carbonate or methyl propargyl carbonate, and another organic compound is 1,3-propanedisultone.

tone, 1,4-butanediol dimethane sulfonate, or ethylene glycol dimethane sulfonate. It is also preferred that one organic compound is benzaldoxime methylcarbonate and another organic compound is divinylsulfone. It is also preferred that one organic compound is a sulfonate compound and another organic compound is a sultone compound. It is also preferred that one organic compound is 1,4-butanediol dimethanesulfonate or ethylene glycol dimethanesulfonate, and another organic compound is 1,3-propanesultone or 1,4-butanediol dimethanesulfonate. It is also preferred that one organic compound is phenylacetylene, and another organic compound is vinylene carbonate, 1,3-propanesultone, or 1,4-butanediol dimethanesulfonate.

It is preferred that the addition of the above-described two or more organic compounds is made to a non-aqueous solvent comprising one or more cyclic carbonates and one or more chain carbonates. Examples of the cyclic carbonates include ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC). Examples of the chain carbonates include dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl ethyl carbonate (MEC), and methyl isopropyl carbonate (MIPC). Other known non-aqueous solvents such as tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 1,2-dibutoxyethane,  $\gamma$ -butyrolactone, acetonitrile, methyl propionate, and dimethylformamide may be incorporated into the mixture of the cyclic carbonate and the chain carbonate. The mixture solvent of the non-aqueous electrolytic solution preferably contains the combination of the cyclic carbonate and chain carbonate at least 60 weight %, more preferably at least 80 weight %, and most preferably at least 90 weight %. In the non-aqueous solvent mixture and in the combination of the cyclic carbonate and the chain carbonate, the cyclic carbonate preferably is in an amount of 5 to 70 volume %, and the chain carbonate preferably is in an amount of 95

to 30 volume %.

In the non-aqueous electrolytic solution of the invention, the combined two or more organic compounds having a reduction potential higher than the non-aqueous solvent are considered to function in the following manner.

In the electric charging stage, the combined organic compounds having a high reduction potential decomposes on the surface of a negative electrode almost at the same time or with a short interval, prior to the decomposition of the solvent material. The products produced by the decomposition of the organic compounds (i.e., additives) deposits on the surface of the negative electrode to cover the surface with an inactive material, which reduces decomposition of the solvent material. If the amount of the additive is larger than a certain level, however, the function of the electrolytic solution lowers.

The non-aqueous electrolytic solution preferably comprises further an electrolyte salt (particularly, inorganic electrolyte salt) such as  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{CF}_3\text{SO}_2\text{Li}$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ ,  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ ,  $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ ,  $\text{LiPF}_4(\text{CF}_3)_2$ ,  $\text{LiPF}_3(\text{CF}_3)_3$ ,  $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$ ,  $\text{LiPF}_5(\text{iso-C}_3\text{F}_7)$ , and  $\text{LiPF}_4(\text{iso-C}_3\text{F}_7)_2$ . The electrolyte salts can be employed singly or in combination. Generally, the electrolyte salt can be incorporated into the non-aqueous solvent in such an amount to give an electrolytic solution of 0.1M to 3M, preferably 0.5M to 1.5M.

The non-aqueous secondary battery of the invention comprises a positive electrode and a negative electrode in addition to the non-aqueous electrolytic solution.

The positive electrode generally comprises a positive electrode active material and an electro-conductive binder composition.

The positive electrode active material preferably is a complex metal oxide containing at least one metal element selected from the group consisting of cobalt, manga-

nese, nickel, chromium, iron, and vanadium and a lithium element. Examples of the complex metal oxides include  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiNiO}_2$ .

5 The electro-conductive binder composition can be produced by a mixture of an electro-conductive material such as acetylene black or carbon black, a binder such as polytetrafluoroethylene (PTFE) or poly(vinylidene fluoride) (PVDF), and a solvent. For the preparation of a positive electrode, the mixture is coated on a metal  
10 plate such as aluminum foil or stainless plate, dried, and pressed for molding. The molded product is then heated *in vacuo* at a temperature of approx. 50 to 250°C for approx. 2 hours, to give the desired positive electrode.

15 The negative electrode comprises a negative electrode active material such as a lithium metal, a lithium alloy, carbonaceous material having a graphite-type crystalline structure which can absorb and release lithium ion, or a complex tin oxide. Examples of the carbonaceous materials include thermally decomposed carbonaceous  
20 materials, cokes, graphites (e.g., artificial graphite and natural graphite), fired organic polymer materials, and carbon fibers. Preferred are carbonaceous materials having a graphite-type crystalline structure in which the  
25 lattice distance of lattice surface (002), namely,  $d_{002}$ , is in the range of 0.335 to 0.340 nm. The negative electrode active material in the powdery form such as carbonaceous powder is preferably used in combination with a binder such as ethylene propylene diene terpolymer  
30 (EPDM), polytetrafluoroethylene (PTFE) or poly(vinylidene fluoride) (PVDF).

There are no specific limitations with respect to the structure of the non-aqueous secondary battery of the invention. For instance, the non-aqueous secondary battery  
35 can be a battery of coin type comprising a positive electrode, a negative electrode, and single or plural



separators, or a cylindrical or prismatic battery comprising a positive electrode, a negative electrode, and a separator roll. The separator can be a known microporous polyolefin film, woven fabric, or non-woven fabric.

5

The present invention is further described by the following non-limiting examples.

[Measurement of Reduction Potential]

10 Ten mg of graphite powder (MCMB6-28, produced by Osaka Gas Chemical Co., Ltd.) is mixed with 10 wt.% of polyvinylidene fluoride (binder). The mixture is placed in N-methylpyrrolidone to give a slurry. The slurry is  
15 coated on a electro-collector stainless steel plate (surface area: 2 cm<sup>2</sup>). Thus coated plate is set as a working electrode to form a triode cell in combination with counter and reference electrodes using lithium metal.

A non-aqueous solvent is prepared from ethylene carbonate and methyl ethyl carbonate at a volume ratio of  
20 3:7. To the solvent is added LiPF<sub>6</sub> (electrolyte, to give 1 M concentration) to produce an electrolytic solution. To the resulting electrolytic solution is added an organic compound (i.e., additive) to be measured, in an amount of 2 wt.%.

25 The triode cell is placed in the additive-containing electrolytic solution, and the reduction potential is measured at room temperature under a potential scanning rate of 1 mV/sec. A potential in terms of V at which a current of 0.5 mA flows is assigned to the reduction po-  
30 tential.

The reduction potentials measured on various organic compounds are set forth in Table 1.

Table 1

	Organic Compound (Additive)	Abbr.	Reduction Potential (vs. lithium metal)
5			
	Vinylene carbonate	VC	0.81 V
	1,3-Propanesultone	PS	0.83 V
	1,4-Butanesultone	BS	0.80 V
10	1,4-Butanediol		
	dimethane sulfonate	BDDMS	0.81 V
	Ethylene glycol		
	dimethane sulfonate	EGDMS	0.81 V
	Methyl propargyl carbonate	MPGC	0.82 V
15	Phenylacetylene	PA	0.81 V
	Benzaldoxime carbonate	BAOMC	1.78 V
	Divinylsulfone	VS	1.45 V

20

[Example 1]

1) Preparation of non-aqueous electrolytic solution

25 In a non-aqueous mixture of propylene carbonate and dimethyl carbonate [PC:DMC=1:2, volume ratio] was dissolved  $\text{LiPF}_6$  to give a non-aqueous electrolytic solution of 1 M concentration. To the electrolytic solution were added vinylene carbonate (VC) and 1,3-propanesultone (PS), both in an amount of 1.5 wt.% (based on the amount of the electrolytic solution).

30 2) Preparation of lithium secondary battery and measurement of its battery characteristics

35  $\text{LiCoO}_2$  (positive electrode active material, 80 wt.%), acetylene black (electro-conductive material, 10 wt.%), and poly(vinylidene fluoride) (binder, 10 wt.%) were mixed. To the resulting mixture was further added N-methylpyrrolidone (solvent). Thus produced positive electrode mixture was coated on aluminum foil, dried, molded under pressure, and heated to give a positive

electrode.

Natural graphite (negative electrode active material, 90 wt.%) and poly(vinylidene fluoride) (binder, 10 wt.%) were mixed. To the resulting mixture was further  
5 added N-methylpyrrolidone (solvent). Thus produced negative electrode mixture was coated on copper foil, dried, molded under pressure, and heated to give a negative electrode.

The positive and negative electrodes, a microporous  
10 polypropylene film separator, and the non-aqueous electrolytic solution were combined to give a coin-type battery (diameter: 20 mm, thickness: 3.2 mm).

The coin-type battery was charged at room temperature (20°C) with a constant electric current (0.8 mA) to  
15 reach 4.2 V, and then the charging was continued under a constant voltage of 4.2 V for a period of 6 hours. Subsequently, the battery was discharged to give a constant electric current (0.8 mA). The discharge was continued to give a terminal voltage of 2.7 V. The charge-dis-  
20 charge cycle was repeated 50 times.

The initial discharge capacity was as much as 0.97 which was calculated on the basis that the initial discharge capacity measured in Comparison Example 6 (using a  
25 solvent mixture consisting of ethylene carbonate, propylene carbonate and diethyl carbonate, 3/1/6, volume ratio) was set to 1.

After the 50 cycle charge-discharge procedure, the discharge capacity was 94.8% of the initial discharge capacity. No deformation was observed on the battery  
30 appearance. The low temperature characteristics were satisfactory.

The preparation and evaluation of the battery are summarized in Table 2.

35 [Comparison Example 1]

The procedures of Example 1 were repeated except

that neither VC nor PS were incorporated into the electrolytic solution.

In performing the charging procedure using the secondary battery, propylene carbonate (PC) decomposed at the first charging procedure, and no discharge was done. The battery was deformed. The battery was then disjointed to examine its interior. The graphite negative electrode showed exfoliation on its surface.

The preparation and evaluation of the battery are summarized in Table 2.

[Comparison Examples 2 to 5]

The procedures of Example 1 were repeated except that only one of VC and PS was incorporated into the electrolytic solution.

The preparation and evaluation of the battery are summarized in Table 2.

Table 2  
(Solvent: PC/DMC=1/2)

Example	Additive(s) (%)	Initial discharge capacity (relative value)	Discharge capacity retention
Example 1	VC(1.5)/PS(1.5)	0.97	94.8%
Com.Ex. 1	None	0	--
Com.Ex. 2	VC(1.5)	0.93	83.2%
Com.Ex. 3	VC(3.0)	0.95	84.8%
Com.Ex. 4	PS(1.5)	0.95	82.7%
Com.Ex. 5	PS(3.0)	0.96	84.3%

[Examples 2 & 3]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/DEC (1/2) (for Example 2), and that the solvent was replaced with EC/MEC (1/2) and the negative electrode was made from artificial graphite (for Example 3).

The preparation and evaluation of the battery are summarized in Table 3.

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Table 3  
(Additive: VC(1.5%)/PS(1.5%))

15

Example	Solvent (graphite)	Initial dis- charge capacity (relative value)	Discharge capacity retention
Example 2	EC/DEC=1/2 (natural)	1.02	95.3%
Example 3	EC/MEC=1/2 (artificial)	1.03	94.7%

20

25

[Examples 4 to 7]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (1/1/2) and that the amount of the added organic compounds were changed.

30

The preparation and evaluation of the battery are summarized in Table 4.

Table 4  
(Solvent: EC/PC/DEC=1/1/2)

5	Example	Additives	Initial dis-charge capacity (relative value)	Discharge capacity retention
10	Example 4	VC(0.5)/PS(1.5)	1.01	93.5%
	Example 5	VC(3.0)/PS(1.5)	0.98	93.8%
	Example 6	VC(1.5)/PS(0.5)	1.00	93.1%
	Example 7	VC(1.5)/PS(3.0)	0.99	93.6%

15

[Examples 8 and Comparison Examples 6 to 9]

20 The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

The incorporation of the additives was examined under various conditions.

25 The preparation and evaluation of the battery are summarized in Table 5.

Table 5  
(Solvent: EC/PC/DEC=3/1/6,  
Negative electrode: artificial graphite)

Example	Additives	Initial dis-charge capacity (relative value)	Discharge capacity retention
Example 8	VC(1.5)/PS(1.5)	1.02	95.5%
Com.Ex. 6	None	1.00	81.6%
Com.Ex. 7	VC(1.5)	0.97	83.8%
Com.Ex. 8	PS(1.5)	1.00	84.2%
Com.Ex. 9	VC(10.0)/PS(10.0)	0.93	80.6%

20

[Example 9]

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The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/MEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

Each of the additives of VC and PS were incorporated in an amount of 2.0 wt.%.

The preparation and evaluation of the battery are summarized in Table 6.

30

Table 6  
(Solvent: EC/PC/MEC=3/1/6,  
Negative electrode: artificial graphite)

Example	Additives	Initial dis-charge capacity (relative value)	Discharge capacity retention
Example 9	VC(2.0)/PS(2.0)	1.03	94.1%

40

[Example 10]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DMC/MIPC (3/1/3/3) and that the natural graphite for the negative electrode was replaced with artificial graphite.

The preparation and evaluation of the battery are summarized in Table 7.

Table 7  
(Solvent: EC/PC/DMC/MIPC (3/1/3/3),  
Negative electrode: artificial graphite)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 10	VC(1.5)/PS(1.5)	1.01	93.4%

[Examples 11 & 12 and Comparison Example 10]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DMC/DEC (3/1/3/3), that  $\text{LiCoO}_2$  (positive electrode active material) was replaced with  $\text{LiMn}_2\text{O}_4$ , and that the natural graphite for the negative electrode was replaced with artificial graphite.

The incorporation of the additive(s) was examined under various conditions.

The preparation and evaluation of the battery are summarized in Table 8.



Table 8  
(Solvent: EC/PC/DMC/DEC (3/1/3/3),  
Positive electrode:  $\text{LiMn}_2\text{O}_4$ ,  
Negative electrode: artificial graphite)

5	Example	Additives	Initial dis-charge capacity (relative value)	Discharge capacity retention
10	Example 11	VC(1.5)/PS(1.5)	1.05	95.5%
	Example 12	VC(1.5)/BS(1.5)	1.05	95.3%
15	Com.Ex. 10	BS(1.5)	1.00	83.4%

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[Examples 13 to 19 and Comparison Examples 11 to 14]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

25

The incorporation of the additive(s) was examined under various conditions.

The preparation and evaluation of the battery are summarized in Table 9.

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Table 9  
(Solvent: EC/PC/DEC (3/1/6),  
Negative electrode: artificial graphite)

5	Example	Additives	Initial dis-charge capacity (relative value)	Discharge capacity retention
10	Example 13	VC(1.5)/PS(1.0) /BS(0.5)	1.03	95.8%
	Example 14	VC(1.5)/BDDMS(1.5)	1.02	94.2%
	Example 15	VC(1.5)/EGDMS(1.5)	1.01	93.7%
15	Example 16	VC(1.5)/BDDMS(1.0) /EGDMS(0.5)	1.02	94.9%
	Example 17	PS(1.5)/BDDMS(1.5)	1.00	93.9%
	Example 18	PS(1.5)/EGDMS(1.5)	1.00	93.3%
	Example 19	PS(1.5)/BDDMS(1.0) /EGDMS(0.5)	1.01	94.5%
20	Com.Ex. 11	BDDMS(1.5)	1.01	82.9%
	Com.Ex. 12	EGDMS(1.5)	1.01	82.3%
25	Com.Ex. 13	BDDMS(3.0)	1.01	83.9%
	Com.Ex. 14	EGDMS(3.0)	1.01	83.1%

30 [Examples 20 to 25 and Comparison Examples 15 to 18]  
The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

35 The incorporation of the additive(s) was examined under various conditions.

The preparation and evaluation of the battery are summarized in Table 10.

Table 10  
(Solvent: EC/PC/DEC (3/1/6),  
Negative electrode: artificial graphite)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 20	VC(1.5)/MPGC(1.5)	1.00	92.3%
Example 21	VC(1.5)/PA(1.5)	1.00	91.5%
Example 22	VC(1.5)/MPGC(0.5) /PA(1.0)	1.01	92.9%
Example 23	PS(1.5)/MPGC(1.5)	1.01	92.0%
Example 24	PS(1.5)/PA(1.5)	1.01	90.9%
Example 25	PS(1.5)/MPGC(0.5) /PA(1.0)	1.02	92.5%
Com.Ex. 15	MPGC(1.5)	1.00	82.0%
Com.Ex. 16	PA(1.5)	1.00	81.9%
Com.Ex. 17	MPGC(3.0)	1.00	83.2%
Com.Ex. 18	PA(3.0)	1.00	82.9%

[Examples 26 to 28 and Comparison Examples 19 to 25]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

The incorporation of the additive(s) was examined under various conditions.

The preparation and evaluation of the battery are summarized in Table 11.

Table 11  
(Solvent: EC/PC/DEC (3/1/6),  
Negative electrode: artificial graphite)

5	Example	Additives	Initial dis- charge capacity (relative value)	Discharge capacity retention
10	Example 26	VS (0.15) /BAOMC (2.0)	1.01	93.8%
	Example 27	VS (0.2) /BAOMC (1.5)	1.00	94.0%
	Example 28	VS (0.3) /BAOMC (1.5)	1.00	92.5%
15	Com.Ex. 19	VS (0.2)	1.00	83.5%
	Com.Ex. 20	BAOMC (1.5)	1.00	83.2%
	Com.Ex. 21	VS (1.7)	0.77	74.7%
	Com.Ex. 22	BAOMC (1.7)	0.99	85.1%
20	Com.Ex. 23	VS (10.0) /BAOMC (10.0)	0.66	63.4%
	Com.Ex. 24	BDDMS (1.5) /BAOMC (1.5)	1.00	83.2%
	Com.Ex. 25	PA (1.5) /VS (0.2)	1.00	83.5%
25				

WHAT IS CLAIMED IS:

1. A non-aqueous electrolytic solution comprising  
5 at least two organic compounds dissolved in a solvent  
comprising a cyclic carbonate and a chain carbonate, in  
an amount of 0.01 to 8 weight % for each compound,

in which both of said two organic compounds have a  
reduction potential higher than those of the cyclic and  
10 chain carbonates, and

in which one of the organic compounds has a reduc-  
tion potential equal to that of another organic compound  
or has a reduction potential lower or higher than that of  
another organic compound by a potential of less than 0.4  
15 V.

2. The non-aqueous electrolytic solution of claim  
1, in which each organic compound is dissolved in the  
solvent in an amount of 0.1 to 4 weight %.

20 3. The non-aqueous electrolytic solution of claim  
1, in which said one organic compound has a reduction po-  
tential equal to that of another organic compound or a  
reduction potential lower or higher than that of another  
25 organic compound by a potential of less than 0.2 V.

4. The non-aqueous electrolytic solution of claim  
3, in which said one organic compound has a reduction po-  
tential equal to that of another organic compound or a  
30 reduction potential lower or higher than that of another  
organic compound by a potential of less than 0.05 V.

5. The non-aqueous electrolytic solution of claim  
1, in which said one organic compound is a carbonate  
35 compound and another organic compound is a sultone com-  
pound, a sulfonate compound, or a sulfone compound.

6. The non-aqueous electrolytic solution of claim 5, in which said one organic compound is vinylene carbonate or methyl propargyl carbonate and another organic compound is 1,3-propanesultone, 1,4-butanessultone, 1,4-butanediol dimethane sulfonate, or ethylene glycol dimethane sulfonate.

7. The non-aqueous electrolytic solution of claim 5, in which said one organic compound is benzaldoxime methylcarbonate and another organic compound is divinylsulfone.

8. The non-aqueous electrolytic solution of claim 1, in which said one organic compound is a sulfonate compound and another organic compound is a sultone compound.

9. The non-aqueous electrolytic solution of claim 8, in which said one organic compound is 1,4-butanediol dimethanesulfonate or ethylene glycol dimethane sulfonate, and another organic compound is 1,3-propanesultone or 1,4-butanessultone.

10. The non-aqueous electrolytic solution of claim 1, in which said one organic compound is phenylacetylene, and another organic compound is vinylene carbonate, 1,3-propanesultone, or 1,4-butanessultone.

11. The non-aqueous electrolytic solution of claim 1, in which the solvent comprises 5 to 70 volume % of the cyclic carbonate and 95 to 30 volume % of the chain carbonate.

12. The non-aqueous electrolytic solution of claim 1, in which the cyclic carbonate is selected from the group consisting of ethylene carbonate, propylene carbonate, and butylene carbonate.

13. The non-aqueous electrolytic solution of claim 1, in which the chain carbonate is selected from the group consisting of dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, and methyl isopropyl carbonate.

14. The non-aqueous electrolytic solution of claim 1, which contains an electrolyte salt.

15. A non-aqueous lithium secondary battery which comprises a positive electrode comprising lithium complex oxide, a negative electrode comprising graphite, a non-aqueous electrolytic solution containing an electrolyte salt in a non-aqueous solvent, and a separator, in which the non-aqueous electrolytic solution comprises at least two organic compounds dissolved in a solvent comprising a cyclic carbonate and a chain carbonate, in an amount of 0.01 to 8 weight % for each compound, in which both of said two organic compounds have a reduction potential higher than those of the cyclic and chain carbonates, and in which one of the organic compounds has a reduction potential equal to that of another organic compound or has a reduction potential lower or higher than that of another organic compound by a potential of less than 0.4 V.

16. The non-aqueous lithium secondary battery of claim 15, in which each organic compound is dissolved in the solvent in an amount of 0.1 to 4 weight %.

17. The non-aqueous lithium secondary battery of claim 15, in which said one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.2 V.

18. The non-aqueous lithium secondary battery of claim 15, in which said one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.05 V.

19. The non-aqueous lithium secondary battery of claim 15, in which said one organic compound is a carbonate compound and another organic compound is a sultone compound, a sulfonate compound, or a sulfone compound.

20. The non-aqueous lithium secondary battery of claim 19, in which said one organic compound is vinylene carbonate or methyl propargyl carbonate and another organic compound is 1,3-propanesultone, 1,4-butanessultone, 1,4-butanediol dimethanesulfonate, or ethylene glycol dimethane sulfonate.

21. The non-aqueous lithium secondary battery of claim 19, in which said one organic compound is benzaldoxime methylcarbonate and another organic compound is divinyl sulfone.

22. The non-aqueous lithium secondary battery of claim 15, in which said one organic compound is a sulfonate compound and another organic compound is a sultone compound.

23. The non-aqueous lithium secondary battery of claim 22, in which said one organic compound is 1,4-butanediol dimethanesulfonate or ethylene glycol dimethane sulfonate, and another organic compound is 1,3-propanesultone or 1,4-butanessultone.



24. The non-aqueous lithium secondary battery of claim 15, in which said one organic compound is phenylacetylene, and another organic compound is vinylene carbonate, 1,3-propanesultone, or 1,4-butanessultone.

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25. The non-aqueous lithium secondary battery of claim 15, in which the solvent comprises 5 to 70 volume % of the cyclic carbonate and 95 to 30 volume % of the chain carbonate.

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26. The non-aqueous lithium secondary battery of claim 15, in which the cyclic carbonate is selected from the group consisting of ethylene carbonate, propylene carbonate, and butylene carbonate.

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27. The non-aqueous lithium secondary battery of claim 15, in which the chain carbonate is selected from the group consisting of dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, and methyl isopropyl carbonate.

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28. The non-aqueous secondary battery of claim 15, in which said graphite is natural graphite or artificial graphite.

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29. The non-aqueous secondary battery of claim 15, in which the graphite has a lattice plane of (002) having a plane distance in term of  $d_{002}$  in a length of 0.335 to 0.340 nm.

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ABSTRACT OF THE DISCLOSURE

10       A non-aqueous electrolytic solution composed of two  
or more organic compounds dissolved in a solvent composed  
of a cyclic carbonate and a chain carbonate, in an amount  
of 0.01 to 8 weight % for each compound, in which both of  
the two organic compounds have a reduction potential  
15       higher than those of the cyclic and chain carbonates, and  
in which one of the organic compounds has a reduction po-  
tential equal to that of another organic compound or has  
a reduction potential lower or higher than that of anoth-  
er organic compound by a potential of less than 0.4 V is  
20       favorably employable for a non-aqueous secondary battery.

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## Declaration and Power of Attorney For Patent Application

### 特許出願宣言書及び委任状

### Japanese Language Declaration

### 日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name.

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者であると（下記の名称が複数の場合）信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

NON-AQUEOUS ELECTROLYTIC

SOLUTION AND LITHIUM SECONDARY

BATTERY

上記発明の明細書（下記の欄でx印がついていない場合は、本書に添付）は、

the specification of which is attached hereto unless the following box is checked:

☐ 月 日に提出され、米国出願番号または特許協定条約国際出願番号を \_\_\_\_\_ とし、  
（該当する場合） \_\_\_\_\_ に訂正されました。

☐ was filed on \_\_\_\_\_  
as United States Application Number or  
PCT International Application Number  
\_\_\_\_\_ and was amended on  
\_\_\_\_\_ (if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されたとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

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私は、米国法典第35編119条(a)-(d)項又は365条(b)項に基づき下記の、米国外の国の少なくとも一カ国を指定している特許協力条約365(a)項に基づき国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

### Prior Foreign Application(s)

外国での先行出願 11-143222	Japan
(Number) (番号)	(Country) (国名)
2000-116327	Japan
(Number) (番号)	(Country) (国名)
(Number) (番号)	(Country) (国名)
(Number) (番号)	(Country) (国名)

私は、第35編米国法典119条(e)項に基づいて下記の米国外の特許出願規定に記載された権利をここに主張いたします。

(Application No.) (出願番号)	(Filing Date) (出願日)
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(Application No.) (出願番号)	(Filing Date) (出願日)
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I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Not Claimed  
優先権主張なし

24/05/1999	<input type="checkbox"/>
(Day/Month/Year Filed) (出願年月日)	
18/04/2000	<input type="checkbox"/>
(Day/Month/Year Filed) (出願年月日)	
	<input type="checkbox"/>
(Day/Month/Year Filed) (出願年月日)	
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(Day/Month/Year Filed) (出願年月日)	

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.) (出願番号)	(Filing Date) (出願日)
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I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

(Status: Patented, Pending, Abandoned) (現況: 特許許可済、係属中、放棄済)
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(Status: Patented, Pending, Abandoned) (現況: 特許許可済、係属中、放棄済)
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith and to take instructions in connection therewith from Yanagawa & Company (list name and registration number)

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(日本語宣言書)

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ること)

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